

## SOLVENT STRUCTURE EFFECTS IN DIPOLE CORRELATION FORCES

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We have obtained an exact expression for the free energy of electrostatic interaction between two planar layers of orientable dipoles imbedded in a structurable dielectric continuum described by a wave-vector-dependent dielectric response function. We show that the orientable dipoles themselves can be described by a special type of non-local dielectric response. The interaction in the case of non-local solvent coupling is much larger than in the case of ordinary, local dielectric.

## 1. Introduction

The accurate theoretical understanding of forces between surfaces carrying dipoles or zwitterions, immersed in an aqueous solution, is becoming progressively more important as the force measurements between neutral phospholipid bilayers become more accurate. These experiments reveal additional features of the interactions, amounting to an anomalously large attractive force, that have hitherto escaped closer interest of the theorists [1]. A common feature of the experimental results on forces acting between neutral bilayers is the existence of a strong, non-electrostatic in origin, hydration force that dominates the total interaction at separations smaller than  $\approx 30 \text{ \AA}$  [2]. It is becoming clear that at least a part of this force should be attributed to the structural, water-mediated interactions between the surfaces, which can be described in the frame of the non-local dielectric response theory [3].

Recently [4] the detailed molecular nature of the interphase between the phospholipid bilayers and the aqueous solution has also come under closer scrutiny, revealing the contribution of additional orientational degrees of freedom of the surface dipoles to the interactions between electro-neutral bilayers. Developing a perturbation formalism for the inter-

action free energy, Attard and Mitchell [4] have been able to establish the existence of an attractive force operating between essentially two-dimensional, orientable, surface dipole layers. The physical basis of this force is the correlated electrostatic interaction between fluctuating dipoles at the polar-apolar interface.

In what follows an attempt will be made to incorporate the water structure explicitly into the model of surface dipole correlation forces. Since the PN dipole in the case of PE and PC<sup>#1</sup> bilayers can fluctuate essentially only in the plane of the bilayer surface [5], the direction of the dipole will be assumed to be perpendicular to the local normal of the bilayer surface. In contrast with the former treatment of the problem, it will be shown that the free energy can be obtained directly, in a closed form, without any need for a perturbation-type treatment. Furthermore, a direct link between surface dipole fluctuations and a special form of the non-local dielectric response will be established, allowing for a straightforward treatment of the solvent structure effect on the same level. The solvent dielectric function will be approximated by the usual Lorentzian expression in the specular reflection approximation. Finally it will be argued that the combined effects of water-structure-mediated surface dipole correlations

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<sup>#1</sup> The abbreviations are: PE, phosphatidylethanolamine; PC, phosphatidylcholine.

lead to the existence of an exponentially decaying attractive force. The direct point of contact between the usual van der Waals forces and the surface dipole correlation forces, not noted by Attard and Mitchell [4], will be commented upon.

## 2. Analysis

The geometry of our system is presented in fig. 1. The two dipolar layers are a distance  $2a$  apart and the dipoles are allowed to fluctuate in the  $(x, y)$  plane. We begin with the observation that if all the local dipole charges are concentrated at the inner (solution) side of the surface, say at  $z=z_0$ , we can write the Poisson equation in the form

$$\text{div } \mathbf{D} = \sigma_p(x, y) \delta(z - z_0), \quad (1)$$

where  $\delta(z)$  is the Dirac delta function,  $\mathbf{D}$  is the dielectric displacement vector, and  $\sigma_p(x, y)$  is the local dipolar surface charge density. Due to the overall electro-neutrality of the dipolar sheet we also have

$$\int_S \sigma_p(x, y) dx dy = 0 \quad (2)$$

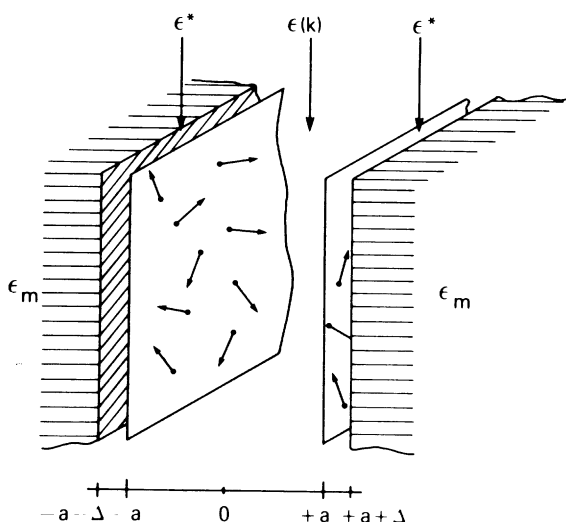


Fig. 1. The geometry of the model. The two dipolar sheets are situated at  $z_0 = \pm a$  and the two semi-infinite dielectrics occupy the space  $|z| > a + \Delta$ . The dielectric constant in the region  $a < |z| < a + \Delta$  is equal to  $\epsilon^*$ . The central dielectric, spanning the space between the two dipolar sheets, is described by a fixed dielectric constant  $\epsilon$  or by a wave-vector-dependent bulk dielectric function  $\epsilon(k)$ .

with  $S$  being the total area. It can be shown quite straightforwardly that, if  $\mathbf{p}(x, y)$  is the local surface dipole density, i.e. surface polarization, we must have

$$\int \rho \sigma_p(\rho) d^2 \rho = \int \mathbf{p}(\rho) d^2 \rho$$

with  $\rho$  being the two-dimensional radius vector ( $\rho = (x, y)$ ). Eq. (1) can be therefore rewritten in an alternative form

$$\text{div } \mathbf{D} = -\text{div}_2 \mathbf{p}(\rho) \delta(z - z_0).$$

Index 2 in the above expression denotes the two-dimensional divergence operator, i.e.  $\partial p_x / \partial x + \partial p_y / \partial y$ . The normal component of the dielectric displacement vector,  $D_n$ , therefore has a discontinuity at  $z = z_0$  equal in absolute value to  $\text{div}_2 \mathbf{p}$ , or formally

$$D_n(\rho, z = z_0 + \epsilon) - D_n(\rho, z = z_0 - \epsilon) = -\text{div}_2 \mathbf{p}(\rho).$$

This is the first equation that we shall make use of in what follows. The second one is an analogue of the macroscopic constitutive equation, connecting polarization in the medium and the imposed electric field. For small enough fields we can assume that the value of surface polarization is proportional to the planar components of the electric field at the point:

$$\mathbf{p}(\rho) = \kappa \mathbf{E}(\rho, z = z_0),$$

where  $\kappa$  is the surface susceptibility. We have supposed that the dipolar layer is isotropic in the plane  $z = z_0$  and only diagonal terms therefore remain in eq. (6). This approximation is, however, optional and can be easily generalized without qualitatively affecting our conclusions.

We proceed now to the calculation of the free energy due to the local orientational fluctuations of surface dipoles. Contrary to the previous work [5] where the device of perturbation expansion was used, we shall exploit the fact that the part of the free energy due to fluctuations can be obtained by a direct coupling constant integration of the appropriate response function. This was shown quite rigorously in the case of standard van der Waals forces by Mitchell and Richmond [6]. Since here we are treating dipolar fluctuations classically, we can confine ourselves to the zero-order frequency term only,

higher terms corresponding to the quantum corrections.

For the sake of simplicity let us limit ourselves to the case where the position of the orientable dipolar layers coincides with dielectric discontinuity ( $z_0 = \pm a$ ,  $\Delta = 0$  in the notation of fig. 1), the aqueous solution having the dielectric constant  $\epsilon$  and the two semi-infinite regions  $\epsilon_m$  respectively. We shall also assume that the values of  $\kappa$  on the two surfaces are the same. Following closely the derivation of ref. [6] we can obtain the free energy appropriate for our system in the form

$$F = F_0 - k_B T \int \frac{d\lambda}{\lambda} \sum_{\alpha=x,y} \left( \int d^2\rho [G_{\alpha}^D(\rho, z = -a) + G_{\alpha}^D(\rho, z = +a)] \right), \quad (7)$$

where  $k_B T$  is the thermal energy,  $\lambda$  the coupling constant,  $F_0$  the part of the free energy not corresponding to dipolar fluctuations, and  $G_{\alpha}^D(\rho, z)$  are the components of the response functions of the two surfaces

$$G_{\alpha}^D(\rho, z) = -\kappa(z) \lim_{\rho \rightarrow \rho'} \frac{\partial^2}{\partial \rho_{\alpha} \partial \rho'_{\alpha}} \phi(\rho, \rho', z). \quad (8)$$

In the above equation  $\phi(\rho, \rho', z)$  is the electrostatic potential at  $\rho$  of a unit point dipole situated at  $\rho'$ . This potential is obtained by solving the Laplace equation with boundary condition (5) and the constitutive relation (6), together with the continuity of the potential at both interfaces. The calculation, though tedious, is straightforward and we shall not repeat it here. Let us just quote the final result

$$\int d^2\rho \sum_{\alpha} [G_{\alpha}^D(\rho, z = -a) + G_{\alpha}^D(\rho, z = +a)] = - \int_0^{\infty} \frac{S}{\pi \epsilon \epsilon_0} Q^2 dQ \frac{\kappa \Delta^+ \Delta^- \exp(-4Qa)}{\Delta^{+4} \det} \quad (9)$$

with the following abbreviations:

$$\Delta^{\pm} = 1 \pm \epsilon_m / \epsilon \pm \kappa Q / 4\pi \epsilon \epsilon_0 \quad (10)$$

and

$$\det = 1 - (\Delta^- / \Delta^+)^2 \exp(-4Qa). \quad (11)$$

The integration over  $Q$  is here, as is usual for the

planar electrostatic problems [7], a consequence of the two-dimensional Fourier transforms in the  $(x, y)$  plane. In deriving eq. (9) we have subtracted that part of the Green function that does not depend on the intersurface separation.

What remains is now the final coupling constant integration in eq. (7). This can be done in the usual way by assuming that  $\kappa$  is a linear function of  $\lambda$  [6], i.e.  $\kappa \rightarrow \lambda \kappa$  and observing that

$$- \frac{4Q\kappa \Delta^+ \Delta^- \exp(-4Qa)}{\epsilon \epsilon_0 \Delta^{+4} \det} = \lambda \frac{\partial \det(\lambda)}{\partial \lambda}. \quad (12)$$

Eq. (7) can now be integrated explicitly and the free energy of the surface dipole correlations can be obtained in a particularly simple form

$$\frac{F}{S} = \frac{k_B T}{4\pi} \times \int_0^{\infty} Q dQ \{ \ln[\det(\lambda=1)] - \ln[\det(\lambda=0)] \}. \quad (13)$$

In the second term of the above expression we can easily recognize the zero-order Lifshitz-van der Waals term [8]. It is therefore appropriate to take  $F_0$  in eq. (7) as equal to this term so that the total free energy of the system equals

$$\frac{F}{S} = \frac{k_B T}{4\pi} \int_0^{\infty} Q dQ \ln[1 - (\Delta^- / \Delta^+)^2 \exp(-4Qa)]. \quad (14)$$

In this way the artificial repulsive component in the free energy, due to the image interactions [4], is exactly cancelled. Assuming now that the dielectric discontinuity at  $z_0 = \pm a$  is absent, we can derive from eq. (12), by expanding it in terms of inverse powers of  $2a$ , the following limiting expression

$$\frac{F}{S} \approx - \frac{3\pi (\kappa k_B T)^2}{8k_B T \epsilon^2 (4\pi \epsilon_0)^2 (2a)^4}, \quad (15)$$

which matches exactly with eq. (6) of ref. [4] if we acknowledge the fact that the definition of the response function used here is slightly different from the one used in ref. [4]. In fact the transformation between the two notations is  $G_{xx}(0) = G_{yy}(0) = \kappa k_B T$ ,  $G_{zz}(0) = 0$ . We shall not pursue the task of showing

that even in the case of isotropic fluctuations not limited to the  $(x, y)$  plane, the exact results obtained by our method reduce in the lowest order to those obtained in ref. [4] provided that the zero-order van der Waals term is added to the expression derived by Attard and Mitchell. What we would like to point out here, however, is that the problem of correlation forces between orientable surface dipole layers can be cast into the language of non-local dielectric response formalism. To show this we shall assume that the dipolar layers (fig. 1) at  $z_0 = \pm a$  are an integral part of the dielectric confined between  $|z| < a + \Delta$  and we shall try to obtain the constitutive relation for this extended dielectric.

Since even the extended dielectric is isotropic in the  $(x, y)$  plane we can certainly write the constitutive relation in the form

$$D_i(Q, z) = \epsilon_0 \int_{-a-\Delta}^{+a+\Delta} \epsilon_{ik}(Q, z, z') E_k(Q, z') dz', \quad (16)$$

where we have introduced the two-dimensional Fourier components

$$\begin{aligned} \epsilon_{ik}(Q, z, z') &= \frac{1}{2\pi^2} \int d^2\rho \epsilon_{ik}(\rho - \rho', z, z') \exp[iQ(\rho - \rho')] \\ & \quad (17) \end{aligned}$$

of the dielectric function and analogously for the electric field and dielectric displacement vector. It can be easily shown that eqs. (5) and (6) can be reproduced if the following form for the dielectric response function of the extended dielectric is assumed:

$$\begin{aligned} \epsilon_{ik}(Q, z, z') &= \epsilon \delta_{ik} \delta(z - z') \\ &+ \kappa (\delta_{ix} \delta_{kx} + \delta_{iy} \delta_{ky}) \delta(z + a) \delta(z' + a) \\ &+ \kappa (\delta_{ix} \delta_{kx} + \delta_{iy} \delta_{ky}) \delta(z - a) \delta(z' - a). \end{aligned} \quad (18)$$

The first term in the above equation clearly corresponds to the usual local dielectric response of the medium. The other two terms, of a particular non-local form, represent the contribution of the two orientable dipolar sheets at  $z_0 = \pm a$  to the total dielectric response of the extended dielectric.

We can therefore reinterpret eq. (14) as the free energy of the usual van der Waals interactions with

the provision that the central dielectric, spanning the whole region between the dielectric discontinuities is described by the dielectric function (18). The energy could therefore be obtained by the usual dipole approach, viz. by calculating the secular determinant corresponding to the dielectric response and then using the Ninham-Parsegian-Weiss theorem to obtain the zero- (frequency) order energy.

If the dielectric between the two sheets bearing orientable dipoles is furthermore characterized by a non-local dielectric response, the generalization of eqs. (18) and (14) is now really straightforward. Let us limit ourselves to the case where the bulk dielectric function of the non-local structurable medium  $\epsilon(k)$ , can be sufficiently well approximated by the usual Lorentzian expression [10]

$$\epsilon(k) = \epsilon_\infty + \frac{\epsilon - \epsilon_\infty}{1 + (\epsilon_\infty/\epsilon) k^2 \xi^2} \quad (19)$$

with  $k$  denoting the three-dimensional wave vector and  $\epsilon_\infty$  the infinite frequency dielectric constant of the medium. We shall use the specular reflection approximation [11] to connect the dielectric response of the bulk dielectric with the dielectric response of the same material intercalated between the two faces at  $z = \pm a$ .

To obtain the free energy of the interaction in this case we follow closely the method of ref. [11], and we have shown above that the dipolar correlation force is nothing but a generalized version of the van der Waals force. In the region  $|z| < a$  the dielectric response is therefore characterized by eq. (18), provided that the term  $\epsilon \delta_{ik} \delta(z - z')$  is substituted by appropriate specular reflection model expression for the bulk response function (19). The regions between  $z = \pm a$  and the two dielectric discontinuities of thickness  $\Delta$  have a local dielectric response characterized by  $\epsilon^*$ . Finally the two semi-infinite regions are described by the dielectric constant  $\epsilon_m$ . The details of the somewhat lengthy but nevertheless straightforward derivation will be published elsewhere. Here we merely quote the final expression for the free energy

$$\frac{F}{S} = \frac{k_B T}{4\pi} \int_0^\infty Q dQ \ln \left( \frac{\text{Det}}{1 - \exp[-4w(a + \Delta)]} \right), \quad (20)$$

where we used the following definitions

$$w^2 = Q^2 + (\epsilon_\infty/\epsilon)\xi^{-2}, \quad (21a)$$

$$u^2 = Q^2 + \xi^{-2}, \quad (21b)$$

and abbreviations

$$\text{Det} = \{1 + \alpha_{11} \exp[-2(u+Q)a]\}^2 - [\alpha_{01} \exp(-2ua) + \alpha_{10} \exp(-2Qa)]^2, \quad (22a)$$

$$\alpha_{ik} = \frac{\epsilon_\infty^{-1} + (-1)^i \Gamma/\epsilon + (\epsilon_\infty^{-1} - \epsilon^{-1})(-1)^k Q\Gamma/u}{\epsilon_\infty^{-1} + \Gamma/\epsilon + (\epsilon_\infty^{-1} - \epsilon^{-1})Q\Gamma/u}, \quad (22b)$$

$$\Gamma = \epsilon^* \delta^- / \epsilon_m \delta^+ + \kappa Q / 4\pi \epsilon_0 \epsilon_m, \quad (22c)$$

$$\delta^\pm = 1 \pm \frac{1 - \epsilon_\infty/\epsilon^*}{1 + \epsilon_\infty/\epsilon^*} \exp(-2Qa). \quad (22d)$$

The integral (20) reduces to the usual zero-order Lifshitz-van der Waals term at large  $a$ . In the opposite limit we have been unable to find any simple analytic approximation and had to analyze eq. (20) numerically.

### 3. Results

We investigated the dependence of attractive pressure, defined as the derivative of eq. (20) with respect to  $2a$ . We have used the model system defined on fig. 1 with  $\Delta = 3 \text{ \AA}$ , corresponding to a layer of water molecules behind the orientable dipole sheet. The dielectric constant of the two semi-infinite regions was assumed to be  $\epsilon_m = 2$ , in correspondence with the dielectric data on the hydrocarbon core of the phospholipid layer [12]. The dielectric constant of the two thin aqueous layers was taken as  $\epsilon^* = \epsilon_\infty$ , since presumably the immobilized water molecules can respond only with the high-frequency dielectric constant, stemming essentially from the electron relaxation and being close to  $\epsilon_\infty = 5$  for water. The static, macroscopic dielectric constant of water,  $\epsilon$  in eq. (19), was taken equal to  $\epsilon = 80$  and the correlation length  $\xi = 3 \text{ \AA}$ . The value of  $\kappa$  was assumed to be equal to the ideal gas expression for dipoles with surface density  $1/75 \text{ \AA}^2$  and dipole moment

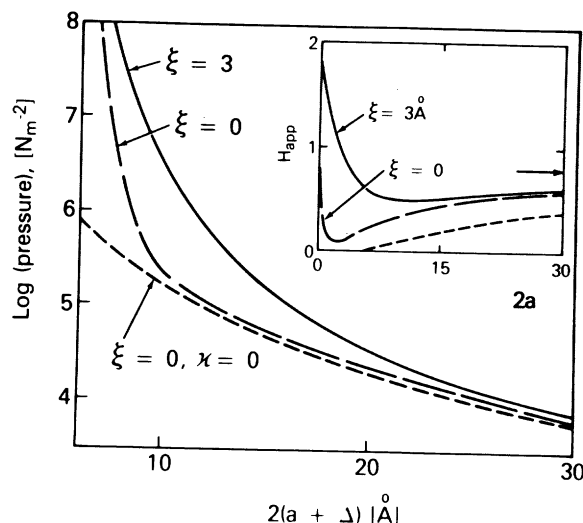


Fig. 2. The logarithm of the attractive pressure as a function of the spacing between the two semi-infinite dielectric regions. The dotted curve corresponds to the standard zero-order Lifshitz-van der Waals result [8] for the interaction of two semi-infinite media of dielectric constant  $\epsilon_m$  interacting across a region with dielectric constant  $\epsilon$ . The dashed curve corresponds to the derivative of eq. (20) with  $\xi=0$  and is an accurated version of the Attard-Mitchell result. The full line is the attractive pressure derived from eq. (20). The value of  $\kappa/4\pi\epsilon_0$  was taken as  $18.5 \text{ nm}$ . The insert presents the apparent Hamaker coefficient (eq. (23)) for the same three cases. The arrow points to the value of the Hamaker coefficient at infinite intersurface spacing. In the case of standard zero-order Lifshitz-van der Waals result the Hamaker coefficient is not a constant, since the plot is made against  $2a$  and not  $2(a+\Delta)$ .

$\mu = 8.0 \times 10^{-29} \text{ A s m}^{1/2}$ , i.e.  $\kappa/4\pi\epsilon_0 = 18.5 \text{ nm}$ .

Fig. 2 presents the results of numerical evaluation of the pressure. We have compared the standard, zero-order Lifshitz-van der Waals term with no contribution from the dipole correlations (dotted line), the derivative of eq. (20) with  $\xi=0$ , which represents an improved version of the Attard-Mitchell [4] result (dashed line), and our result (full line) for the dielectrically non-local central medium. We can see that the dipolar correlations clearly change the behaviour of the pressure at small separations, as was reported in ref. [4], and that the effect of solvent-structure-mediated dipolar correlations is more drastic, amounting to more than an order of mag-

<sup>12</sup> The ideal value of the susceptibility of the two-dimensional dipolar gas is  $\mu^2/k_B T S$ , where  $\mu$  denotes the value of the dipole moment.

nitude even at moderate separations. The changes in the behaviour of pressure as we go from unstructured to structurable dielectric can be understood by analyzing eq. (15). The magnitude of the correlation effect is evidently proportional to  $\epsilon^{-2}$ . If we have a structurable dielectric, e.g. water, its dielectric constant will change from  $\epsilon=80$  at moderate separations to  $\epsilon_{\text{eff}}=\epsilon_{\infty}=5$  at small separations, enhancing thus the magnitude of the correlation effect by two orders of magnitude. Also the correlation effect in the structurable case is not limited only to small intersurface separations but extends furtherout, being appreciable even at separations equal to several correlation lengths.

To explore additional features of solvent-structure-mediated dipolar correlation forces we have plotted the apparent Hamaker coefficient defined as

$$H_{\text{app}} = \frac{12\pi(2a)^2}{k_B T} \frac{F}{S} \quad (23)$$

as a function of  $2a$  in the insert of fig. 2. At large separations  $H_{\text{app}}$  approaches the value specified by the arrow. The dotted curve again corresponds to the standard, i.e. zero-order, Lifshitz-van der Waals term, corrected by the fact that the plot is done against  $2a$  and not  $2(a+\Delta)$ . The full and the dashed line represent the same cases as before. What is particularly conspicuous (and can be made even more evident by plotting  $\log(H_{\text{app}})$  from the insert) is that in the case of non-local, solvent-mediated correlations the apparent Hamaker coefficient in the regime  $a \leq \xi$  is an exponential function of  $2a$ , with the decay length somewhat smaller than  $\xi$  ( $\approx 2 \text{ \AA}$  for  $\xi = 3 \text{ \AA}$ ) and weakly dependent on the value of  $\kappa$ . The surface properties, embedded in the value of  $\kappa$  and the properties of bulk solvent (correlation length  $\xi$ ) are therefore not separable as is the case in the hydration force theory [3]. The solvent-mediated dipolar cor-

relation forces intertwine both characteristics of the system in such a way that surface properties influence not only the magnitude but also the decay of the forces. We are currently trying to interpret the results of the force measurements in the light of the theoretical developments presented here.

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